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Optimization and Performance parameters for adsorption of Cr⁶⁺ by microwave assisted carbon from *Sterculia foetida* shells

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Abstract. Modeling of adsorption of Cr⁶⁺ on to activated carbon prepared from *Sterculia foetida* dried seed shells under different drying techniques namely sun, oven, and microwave drying (450W, 600W, 900W power). Optimization of process parameters such as pH, adsorbent dosage (g/ml), temperature (°C), contact time (min) were evaluated using Central Composite Rotatable Design (CCRD) of Response Surface Methodology (RSM). For batch adsorption studies at pH 3, adsorbent dosage of 1.5 g/ml, temperature 35°C and contact time 90 min were found to be optimum for the system under consideration and Microwave Activated Carbonized *Sterculia foetida* (MACSF) at 450W was found to be best suited for the adsorption of Cr⁺⁶ ions. The system was found to follow Langmuir type monolayer adsorption for the given operational parameters. SEM analysis was used to study the surface morphology of the carbon samples and the effect of pretreatment on carbonization.

1. Introduction

Metals and their derivatives are very harmful when released into the atmosphere and can be particularly problematic due to their stability and mobility. The hexavalent chromium (Cr⁺⁶) in effluents generated from various industries, such as electroplating, steel making, leather tanning, mining etc., is a major concern due to its adverse effects to human health and other living organisms [1]. Hexavalent [Cr⁺⁶] ions are highly toxic and can lead to mutagenic and carcinogenic health hazards[2]. Numerous techniques have been practiced to eliminate Cr⁺⁶ ions from wastewater, the principal processes being chemical processes [3,4], ion exchange [5], membrane separation [6] and adsorption [7]. Adsorption is one of the most promising and technically feasible methods as it involves low cost adsorbents to remove heavy metal ions because of its high affinity for trace ions.

In order to make the process of adsorbent activated carbon preparation more attractive in terms of production costs, various bio-waste materials have been used as low-cost precursors. *Sterculia foetida*, a soft wooded tree that can grow up to 115 feet tall, is such a material found in abundance in most parts of Southern India and hence easily available. Compared to the conventional heating methods, microwave heating has been used as energy source in the preparation of activated carbon from several biomasses [8-11]. Among several advantages, microwave-assisted activation method leads to a more efficient carbonization, resulting in a material with higher surface area and well-developed porosity [8-11].

In the present study, carbon made from seed shells of *Sterculia foetida* was used as adsorbent to remove chromium ions from waste water sources. Further, the effects of the process parameters such as pH, adsorbent dosage, temperature, contact time and initial concentration on removal of Cr⁶⁺ were



investigated and optimized by the application of the Response Surface Methodology (RSM), which is a combination of mathematical and statistical tool. Since conventional method of optimizing the process variables requires a very large number of experimental runs, which is highly expensive and time consuming, RSM is used for developing, improving and optimizing the process variables and to evaluate the relative significance of several process parameters in the presence of complex interactions. In order to have better understanding of the adsorption characteristics Langmuir and Freundlich isotherm models at various operating parameters were studied.

2. Materials and methods

Fresh sterculia flowers were collected from VIT University, Vellore Tamilnadu India. The shells were further taken for drying and used for preparing activated carbon discarding the seeds. *Sterculia foetida* shells were subjected to drying to remove all the moisture content under five different conditions which include direct sun drying, oven drying and microwave drying of three different powers (450W, 600W, 900W) before carbonization.

Dried sterculia samples were broken into uniform size (1inch pieces) and sealed in earthen pots. The pots were kept in a muffle furnace and heated from room temperature to 550°C at an increment of 10°C/min and was held at 550°C for 2 h. The carbon samples obtained were cooled to room temperature. The ash formed while carbonization was removed by washing the samples thoroughly with double distilled water. The wet carbon samples were dried in an oven drier for 24 h at 110°C for further use as adsorbent.

A stock solution of Cr⁶⁺ (1000 mg/L) was prepared from potassium dichromate salt by adding 2.829 g of K₂Cr₂O₇ in 1000 mL distilled water. Other working solutions of different concentrations were also prepared by appropriate dilution of the stock solutions.

2.1. Batch adsorption studies

The adsorption experiments were carried out in batch mode by mixing a specific amount of adsorbent in 50 mL of Cr⁶⁺ solution under constant shaking (120 rpm) in a thermostat shaker. The effects of contact time, amount of adsorbent, initial Cr⁶⁺ concentration, pH and temperature of the solutions were investigated. The samples were analyzed using UV-visible spectrophotometer to estimate the Cr⁶⁺ ion concentration in the solution at 540nm against a standard curve already plotted.

2.2. Experimental optimization

The experimental optimization was done for batch adsorption studies on different activated carbon samples in order to find out the best pre-treatment method for carbonizing that has the maximum adsorption capacity. Simultaneously, the parameters which include pH, adsorbent dosage, temperature, contact time and initial concentration were also optimized. The amount of Cr⁶⁺ adsorbed at equilibrium q_e (mg/g) was calculated using (1).

$$q_e = \left(\frac{(C_0 - C_e)V}{W} \right) \quad (1)$$

$$\% \text{ removal} = \left(\frac{(C_0 - C_e)}{C_0} \times 100 \right) \quad (2)$$

where C_0 and C_e are the initial and equilibrium liquid phase concentrations of Chromium. V is the volume of the solution and W is the mass of the adsorbent.

2.3. Central Composite Rotary Design (CCRD)

Response surface methods (RSM) provide superb statistical design tools and analysis of experimental runs aimed at process optimization. CCRD was used because of its ability to analyze the complex

interaction between process parameters. The CCRD was employed to fit a quadratic equation by multiple regression method which needs a minimum number of experimental test runs for modeling.

The CCRD model consists of a 2^n factorial runs (\pm notations) with $2n$ axial runs ($\pm \alpha, 0 \dots 0$), $(0, \pm \alpha, 0 \dots 0)$, \dots , $(0, 0, \dots, \pm \alpha)$ and n_c center runs (six replicates, $0, 0, \dots, 0$). As the number of factors n increases the number of experimental runs for a complete replicate design also increases according to the following relation

$$N = 2^n + 2n + n_c \quad (3)$$

An empirical model was developed so as to correlate the response to the adsorption of Cr^{6+} on to MACSF based on second order polynomial that follows the equation below;

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \sum_{j=1}^n \beta_{ij} X_i X_j \quad (4)$$

where Y is the predicted response, β_0 is the constant coefficient, β_i is the linear coefficient, β_{ij} is the interaction coefficient and β_{ij} is the quadratic coefficient and X_i, X_j are the coded.

3. Results and discussions

3.1. Batch adsorption studies

3.1.1. Optimization of drying pre-treatments. Among the drying processes considered maximum adsorption capacity of 71% removal was obtained for microwave activated carbonized *Sterculia foetida* (MACSF) at 450W (figure 1). In general, microwave drying had a better efficiency in Cr^{6+} removal compared to other drying processes. The chemical bonds can be vigorously vibrated and ruptured by microwave heating, enhancing the pore structure by molecular diffusion thus leading to higher adsorption in the thermo-chemical process.

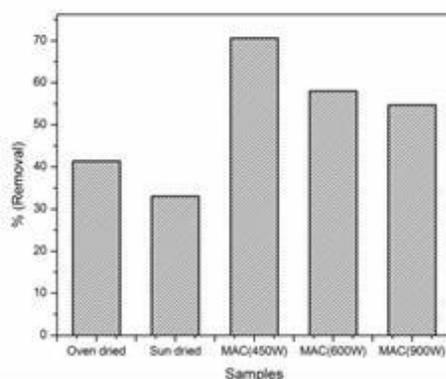


Figure 1. % Removal of Cr^{6+} for different

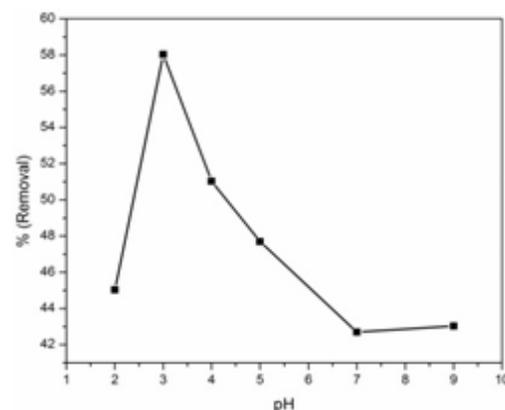


Figure 2. Effect of pH on % removal. activated carbon samples

3.1.2. Effect of pH. The effect of pH on chromium removal is shown in figure 2. The adsorption of chromium increased from 45.4% to 58.4% for increase in pH from 2 to 3. For pH from 3 to 9 adsorption capacity tremendously decreased indicating a strong dependency on pH. The maximum adsorption capacity for the chromium ions occurred at pH 3. As reported earlier, acidic pH is more

effective for Cr^{6+} adsorption [12].

3.1.3. Effect of adsorbent dosage. Different dosages (0.5 g, 1 g, 1.5 g, 2 g) of activated carbon were prepared in 50 mL of chromium solution at pH 3 at room temperature. Figure 3 demonstrated that adsorption increased with increase in adsorbent dosage due to greater availability of pores and surface area of the adsorbent. The significant increase was observed when dosage was increased from 0.5 g to 1.5 g. The maximum adsorption capacity of 61.3% removal of Cr^{6+} was obtained at adsorbent dosage 1.5g/50mL. Equivalent trends in Cr^{6+} adsorption were reported by other researchers [13].

3.1.4. Effect of temperature. The chromium solution at pH 3 and adsorbent dosage of 1.5g/50mL was fixed and prepared. The samples were kept in rotary shaker at different temperatures (30°C, 35°C, 40°C, 45°C) for 2 h at 150 rpm. From figure 4, it is observed that the maximum adsorption capacity of 65% removal was found to be at temperature 35°C. The significant increase in percent removal from 45% to 66% was observed when temperature was increased from 30°C to 35°C.

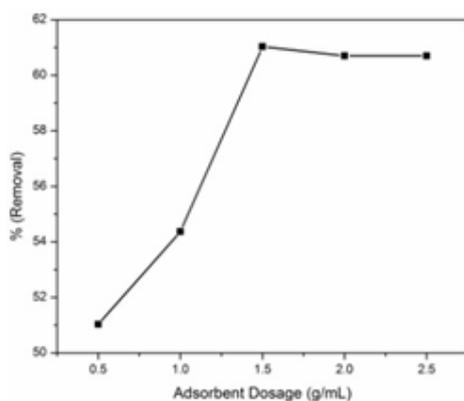


Figure 3. Effect of adsorbent dosage on % removal.

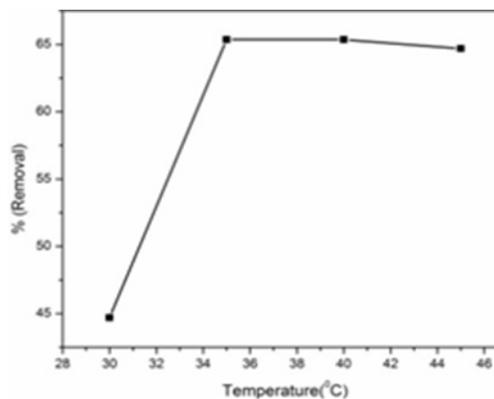


Figure 4. Effect of temperature on % removal.

3.1.5. Effect of contact time. The time dependency was planned at pH 3, adsorbent dosage of 1.5g/50mL and temperature at 35°C process condition as maximum adsorption was attained at these levels. The effect of contact time was correlated for the adsorption of Cr^{6+} ions at regular time intervals ranging from 30min. to 180 min. Figure 5 revealed that the % removal increased and became constant after 90 min. The maximum adsorption capacity of 64.6% removal was observed at 90 min.

3.1.6. Effect of initial concentration. The effect of initial concentration in the range of 300 mg/L to 600mg/L on adsorption was investigated under specified conditions (pH 3, dosage 1.5g/50mL, temperature 35°C, Contact time 90 min.) as shown in figure 6. It was observed that the amount of chromium removed is dependent on initial concentration; at low initial concentration of adsorbate increased percent removal of Cr^{6+} ions was observed. The maximum removal was obtained at 300 mg/L which was 70.11%.

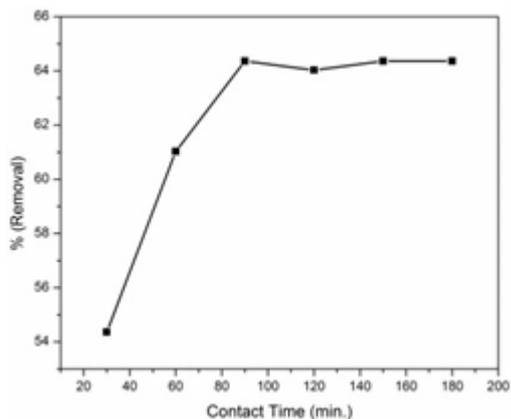


Figure 5. Effect of contact time on % removal

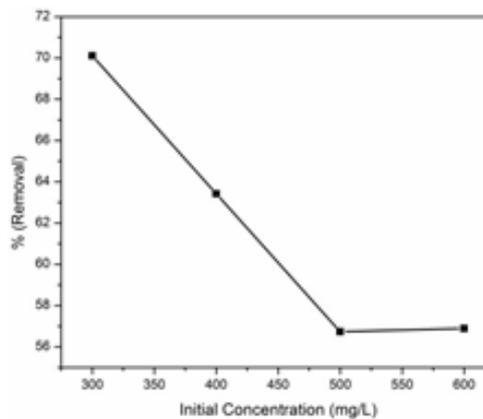
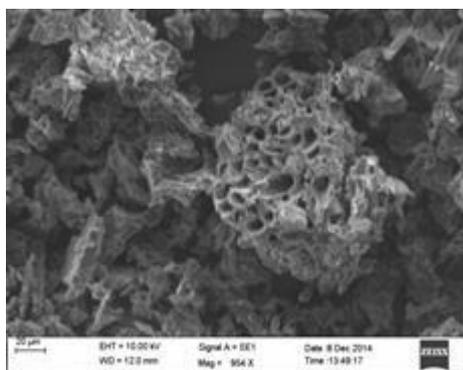
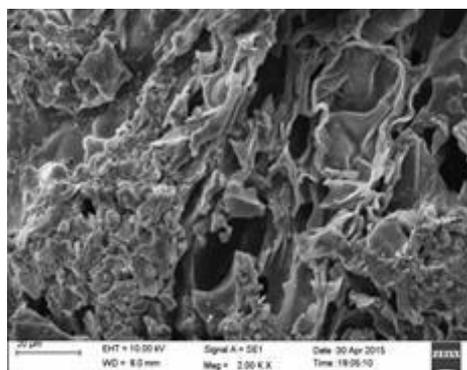


Figure 6. Effect of initial concentrations on % removal

3.1.7. Characterization. The surface morphology and developed pores for the carbonized samples were analyzed using Scanning electron microscope (SEM) with 20kV electron source, make Zeiss EV018 High resolution SEM, Germany. The SEM images figure 7a for Sun dried sample of *Sterculia foetida* showed few active sites on the periphery whereas the image of MACSF figure 7b had irregular surfaces. This is considered helpful for the diffusion of Cr^{+6} ions to activated carbon, as greater the surface area of pores more will be adsorption. From figure 7b and figure 7c, it is observed that the pores present in figure 7b were not visible in figure 7c suggesting a great deal of crystal being adhered to the surface. Thus, these images prove that Cr^{+6} ion was adsorbed by activated carbon into its pores and developed a layer of Cr^{+6} ions on the surface.



(a)



(b)

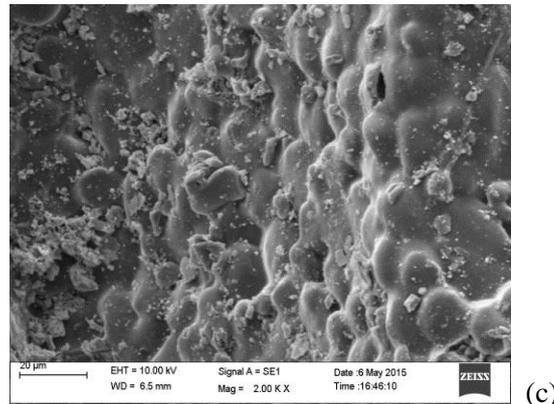


Figure 7. SEM images of (a) Sun Sterculia carbon dried, (b) MACSF (450MW) before adsorption, and (c) MACSF (450MW) after adsorption.

3.1.8. Isotherm models. Adsorption isotherm studies are based on the assumptions that relate homogeneity and heterogeneity of adsorbents, type of coverage and possibility of interaction between adsorbate species. The equilibrium adsorption data were tested for suitability for Langmuir and Freundlich isotherm plot (table 1 & table 2).

Langmuir model equation is given as follows

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \quad (5)$$

where q_m and K_L are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively.

The Freundlich isotherm is an empirical model based on adsorption on heterogeneous surface and is given by the following equation

$$\log q_e = \log K_L + \frac{1}{n} \log C_e \quad (6)$$

where K_f and n are the Freundlich constants, the characteristics of the system. K_f and n are the indicators of the adsorption capacity and adsorption intensity, respectively.

The Tempkin isotherm model is based on the assumption that the decline of the heat of adsorption as a function of linear rather than logarithmic, as given by the Freundlich isotherm. A linear form of the Tempkin model is expressed as

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \quad (7)$$

$$q_e = B \ln A + B \ln C_e \quad (8)$$

Where $B = \frac{RT}{b}$, R is gas constant (8.314 J/molK-1) and T is temperature (in K)

The linearized plot for Langmuir, Freundlich and Tempkin equations are plotted (fig. 8-10). Table 1 with R2 value of 0.93 suggests a Langmuir monolayer type of adsorption with adsorption capacity of 32.7963 mg/g, at 35°C compared to R2 value of 0.88 for Freundlich. This is in accordance with other reported literature [14].

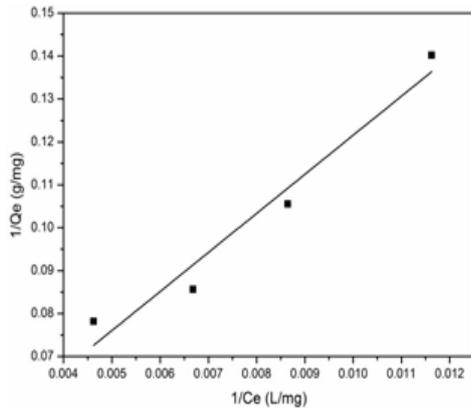


Figure 8. Langmuir isotherm plot at 35⁰C.

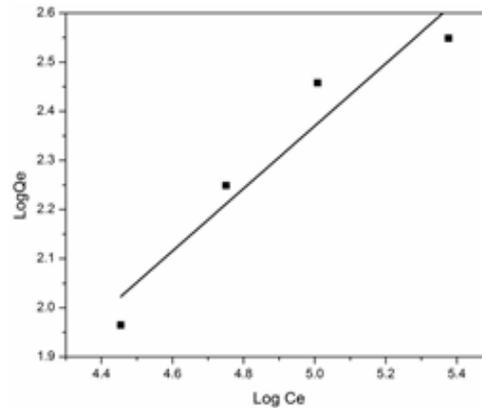


Figure 9. Freundlich Isotherm plot at 35⁰C.

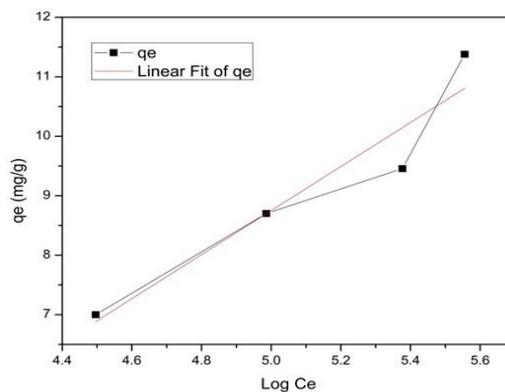


Figure 10. Tempkin isotherm plot at 35⁰C

Table 1 Isotherm Model Factors

Isotherm	Parameters	Parameter values
Langmuir	Coefficient of determination(R ²)	0.9399
$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e}$	Maximum adsorption capacity(q _m)	32.7963 (mg g ⁻¹)
	Energy Constant(Langmuir) K _L	0.003381 (L mg ⁻¹)
Freundlich	Separation Factor(R _L)	0.22
$\log q_e = \log K_f + \frac{1}{n} \log C_e$	Coefficient of determination(R ²)	0.8861
	Adsorption Intensity(n)	1.571
	Freundlich Isotherm constant(K _f)	0.442 (L mg ⁻¹)
Tempkin	Coefficient of determination(R ²)	0.907
$q_e = B \ln A + B \ln C_e$	Constant related to heat of sorption (B)	6.07831 (J/mol)
	Equilibrium Binding constant (A)	0.04128

From the above studies, it was concluded that monolayer adsorption took place as Langmuir isotherm best fits the experimental data.

3.1.9. Optimization studies. The standard RSM design known as CCRD (Central Composite Rotatable Design) was employed to determine the optimum process variables for adsorption of Cr⁶⁺ on MACSF using software (Design Expert 9.0). The CCRD of 3 variables 5 levels; plus and minus alpha (axial points), plus and minus 1 (factorial points) and the center point are taken as independent variables as shown in table 2.

Table 2. Range of optimization variables

Variables	Temperature °C X_1	Adsorbent Dosage g/mL X_2	Contact Time Min X_3
Low	30	1	60
High	40	2	120
+ α	43.41	2.34	140.45
- α	39.55	0.66	26.59

From table 3, R² value for the model is calculated to be 0.98 which signifies that the generated model is in agreement with the experimental results, as revealed by fig 10 -13. "Adeq Precision" measures the signal to noise ratio with a ratio greater than 4 as desirable. This ratio of 21.680 indicates an adequate signal and the fitting of data to the model. This model can be used to navigate the design space with the parametric ranges chosen. Further, from ANOVA, a high significance of the regression model was suggested because of the low probability P value (<0.0001) with the F value for the model at 71.36 implying that this model is significant for adsorption capacity design. There is only a 0.01% chance that an F-value this large could occur due to noise.

The optimum is found to be maximum adsorption capacity of 31.432 mg/g at temperature 34.3°C, adsorbent dosage 1.576g/50mL and contact time 101.266 min with 99.15 desirability. This is comparable to results reported by Sun et al (12).

Table 3 ANOVA

PRESS	34.53
R-Squared	0.9847
Adj R-Squared	0.9709
Pred R-Squared	0,8586
Adeq Precision	21.68

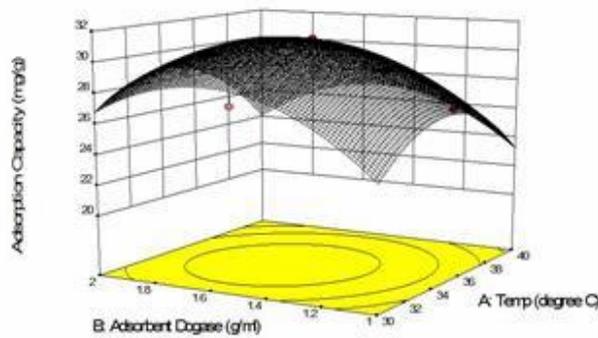


Figure 10. RSM for adsorbent dosage vs. temperature

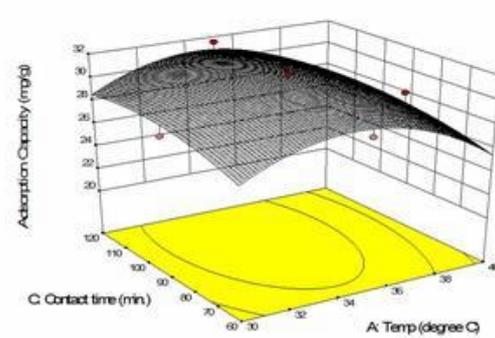


Figure 11. RSM for contact time vs. temperature

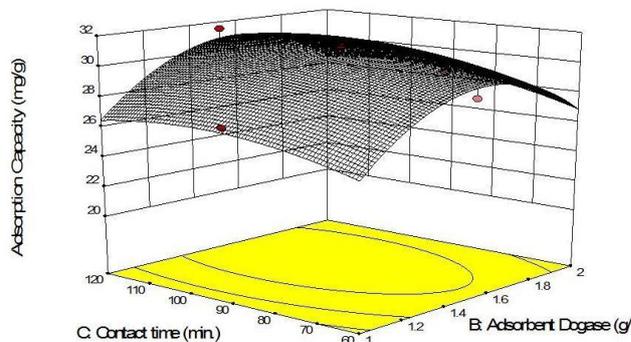


Figure 12. RSM for contact time vs. adsorbent dosage.

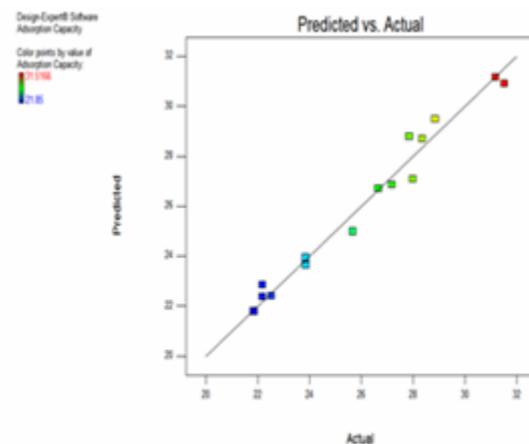


Figure 13. Predicted vs. actual adsorption capacity

The regression equation for the system under consideration was evaluated as

$$\text{Adsorption capacity } Y = -175.25 + 9.19471X_1 + 48.612X_2 + 0.214X_3 - 0.198X_1X_2 - 2.68E-04X_2X_3 + 8.264E-03X_3X_1 + 0.129X_1^2 - 13.532X_2^2 - 1.074E-03X_3^2$$

The analysis of the regression model suggested a quadratic relation with a clear optimum. The interaction between the parameters was negligible as observed with a very low coefficient with an insignificant contribution to the outcome of the relation but the interaction between temperature and dosage showed a negative effect. Temperature was assessed to be one prominent parameter.

4. Conclusions

The effectiveness of using microwave assisted *Sterculia foetida* activated carbon for the removal of Cr^{6+} ions from aqueous solutions was studied. The experimental optimization of batch adsorption parameters revealed maximum adsorption at pH 3, adsorbent dosage 1.5 g/50mL, temperature 35°C for a contact time of 90 minutes and initial concentration at 300 ppm. Langmuir and Freundlich equations were used to describe the adsorption of Cr^{6+} onto prepared activated carbon. Langmuir has

better correlation coefficient than Freundlich model in the concentration studied at different temperatures. The optimized process conditions for the removal of Cr (VI) ions under adsorption onto MACSF adsorbent is predicted using RSM as an effective tool for optimizing process variables.

Acknowledgments

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